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BITUMINOUS MATERIALS AND THE METHOD OF PREPARING THE SAME

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This invention relates to improved homogeneous bituminous materials and to the method of obtaining the same, and more specifically the invention pertains to homogeneous bituminous materials, e. g., asphalts, having a negative spot test, and to the method of obtaining the same from a bituminous material normally having a positive spot test.

Bituminous materials, such as asphalts, cut-back asphalts and road oil residuums, used in the construction of asphaltic roadways and for other purposes are frequently required to pass a test which is indicative of the homogeneity of the product used. This test, popularly known as the "spot test," is often referred to as the "Oliensis test" and less frequently as the "homogeneity test." This test (fully described in the A. S. T. M. Proceedings, volume 33, part II [1933], A. S. T. M. Proceedings, volume 36, part II [1936] in Abraham Asphalts and Allied Substances, page 782 [Test 2D], and in American Association State Highway Officials, Standard Specifications for Highway Materials and Method of Sampling and Testing, part II, Designation T102-42 [1942]) is carried out in the following manner: Two grams of the bituminous materials to be tested are placed in a flask and dissolved in 10.2 cc. of a special naphtha, designated "Spot Test Naphtha," meeting the following requirements:

A. P. I. gravity	49–50.
Initial boiling point	Not less than 300° F.
50% distillation point	335° F. to 355° F.
End point	Not over 410° F.
Aniline number (A. S. T. M. 91–33)	59° C. to 63° C.

The flask and contents may be warmed and when the sample appears to be dissolved, the flask is set aside for thirty minutes and permitted to cool to room temperature. The contents of the flask are mixed by vigorously swirling the flask and three drops of the solution placed on a clean Whatman filter paper, care being taken that the spots do not run together. After five minutes, the spots are examined in a good diffused light. If the drops form a brown or yellowish circular stain with a darker solid or annular nucleus in the center, the spot test is reported as "positive" and the solution in the flask is discarded. However, if the drops form a uniformly brown circular stain, it is reported as "negative" and the filter paper preserved for subsequent comparative test purposes. The flask containing the solution of bituminous materials being tested is stoppered and set aside out of strong light for a period of

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twenty-four hours. At the end of this period the solution is again mixed and stirred with a clean glass rod. Three more drops of the solution are then placed on the filter paper previously used, and after five minutes, examined. If the drops from the twenty-four hour old solution still form a uniformly brown circular stain, the spot test is said to be "negative." However, if the drops form a brown or yellowish brown circular stain with a darker solid or an annular nucleus, the spot test is reported as "positive." In order to meet specifications, the bituminous material being tested must show a "negative" spot test. At times the bituminous material having a negative spot test will be referred to and classified as "homogeneous" while the product which has a positive spot test will be referred to and classified as "heterogeneous."

It is an object of the present invention to provide a bituminous composition having a negative spot test. Another object of the invention is to provide a negative spot test bituminous composition containing a bituminous material normally having a positive spot test. A further object of the invention is to provide a homogeneous asphalt having a negative spot test employing as a major component thereof a bituminous material normally having a positive spot test. A still further object of the invention is to provide a method of correcting heterogeneity in asphaltic materials. Still another object of the invention is to provide a method for converting positive spot test asphaltic materials to negative spot test asphaltic materials. Other objects and advantages of the present invention will become apparent from the following description thereof.

In accordance with the present invention bituminous materials, such as asphalts, cut-back asphalts and other crude petroleum residuum, which normally exhibit a positive spot test when subjected to the hereindescribed test, are converted to products which will give a negative spot test by the addition of a small but sufficient quantity of the propane-insoluble asphaltic resins obtained in the propane deasphalting of a reduced crude petroleum oil, normally having a negative spot test. We have found that as little as 0.5%, by weight, of these asphaltic resins will convert a normally positive spot test bituminous material to a negative spot test product. Usually, from about 0.5% to about 15% of the propane-insoluble asphaltic resins will be found sufficient for the purpose herein described; although, larger quantities, such as 30% to 40%, can be used so long as the desired properties of the bituminous mate-

rial are not adversely affected. For most positive spot test asphaltic materials, from about 0.5% to about 10% of the propane-insoluble asphaltic resins will be found adequate for the conversion of a positive spot test bituminous material to a negative spot test material.

The propane-insoluble asphaltic resins employed in the present invention are obtained in the propane-deasphalting of petroleum residuums which normally exhibit a negative spot test. Propane deasphalting is a process for the removal of asphalts and asphaltic materials from reduced petroleum crude oils or petroleum residuums. The process, well known in the art, is a liquid-liquid extraction process involving the contacting of the reduced crude oil or residuum with liquefied propane, separating of the resultant propane-oil and the propane-insoluble asphaltic resin phases and the recovery of the propane therefrom. The extraction with the liquefied propane may be carried out either stagewise or countercurrently. In conventional processes for the deasphalting of reduced petroleum crude oils a propane to oil charge ratio of from about 1.5 to about 5 parts of propane to each part of oil charged is employed, using temperatures in the range of from about 100° F. to about 150° F., and pressures within the range of from about 200 to about 500 pounds per square inch gauge. The process for the deasphalting of reduced petroleum oils is well known and is described in U. S. Patents Nos. 1,944,491; 1,949,989; 2,041,275; 2,081,473, and others. While liquefied propane is the material usually used in conventional deasphalting processes, other liquefied normally gaseous hydrocarbons, such as methane, ethane and butane can be used. We have found that the propane-insoluble asphaltic resins obtained by the propane deasphalting from any 18% to 40% reduced crude oil can be satisfactorily employed for the herein-described invention provided the reduced crude exhibits a negative spot test. The herein described invention, however, is not limited to the propane-insoluble asphaltic resins from 18% to 40% reduced crude, but includes the use of asphaltic material from any process in which a liquefied normally gaseous hydrocarbon is employed to precipitate insoluble asphaltic resins from a reduced crude petroleum oil or petroleum residuums which exhibits a negative spot test.

The present invention provides a method for correcting the heterogeneity of any asphalt and/or residuum whereby such materials are converted from a positive spot test product to a negative spot test product. We have found the asphaltic resins of the type herein described are effective in correcting the heterogeneity of any oxidized or unoxidized asphalt, or residuum, such as for example, positive spot test asphalts and residuums from low sulfur Mid-Continent crude oils, low sulfur Mid-Continnent-type crude oils, high sulfur West Texas crude oils, high sulfur Wyoming crude oils, and others.

The effectiveness of asphaltic resins of the type herein described in converting positive spot test bitumen materials to negative spot test products is illustrated by the following examples which are given by way of illustrating the invention, and are not to be construed as limiting the scope thereof.

EXAMPLE I

An asphalt, obtained by reducing 38% West Texas crude oil residuum to an asphaltic bottoms having a softening point of 100° F. to 110° F., exhibited a positive spot test. To portions of this asphalt were added 0.5%, 1%, and 2% of propane-insoluble asphaltic resins obtained by propane deasphalting a 25% reduced bottoms of a Mid-Continent crude oil of low sulfur content. The asphaltic resin had a softening point of about 117° F., a penetration at 77° F. of about 65, and a flash (C. O. C.) of about 480° F. Each of the resultant blends exhibited a negative spot test.

EXAMPLE II

An asphalt having a softening point of 100° F. to 110° F., obtained by the reduction of a West Texas crude oil of high sulfur content and which exhibited a positive spot test was blended as in Example I with 0.5%, 1% and 5% of asphaltic resins of the type used in Example I. The results obtained are shown in the following table:

Table I

Sample	Spot Test
West Texas Asphalt	Positive.
West Texas Asphalt+0.5% Propane-Insoluble Asphaltic Resin.	Do.
West Texas Asphalt+1.0% Propane-Insoluble Asphaltic Resin.	Do.
West Texas Asphalt+5.0% Propane-Insoluble Asphaltic Resin.	Negative.

The spot test of this West Texas asphalt was more severely "positive" than that of Example I and therefore required a larger amount of the propane-insoluble asphaltic resin to convert it to a product having a negative spot test.

EXAMPLE III

A residuum from Steamboat Butte Tensleep crude oil having a positive spot test was converted to a product exhibiting a negative spot test when mixed with 10% of a propane-insoluble asphaltic resin such as is used in Example I. The residuum from the Steamboat Butte crude oil had a Furol viscosity at 180° F. of approximately 435 seconds.

EXAMPLE IV

The residuum of Example III when mixed with 10% of the propane-insoluble asphaltic resin having the following inspection gave a product having a negative spot test.

Softening point	174° F.
Penetration at 77° F	4.
Flash (C. O. C.)	580° F.

EXAMPLE V

A blend of 85% of a residuum from a high sulfur Wyoming crude oil and 15% of a residuum from a Steamboat Butte Tensleep which had a positive spot test was converted to a product having a negative spot test by the addition of 5% of the propane-insoluble asphaltic resin of the type used in Example IV.

EXAMPLE VI

Blends consisting of 70% of the Wyoming crude oil residuum and 30% of the Steamboat residuum and blends of 60% of the Wyoming residuum and 40% of the Steamboat residuum, each showing a positive spot test were converted to products having a negative spot test by the addition of 10% of the asphaltic resin of Example IV. The Wyoming crude oil residuum and the Steamboat residuum used in the above blends each had a Furol viscosity at 180° F. of approximately 435 seconds.

EXAMPLE VII

To determine the effectiveness of the present

invention in correcting the spot test of cracked asphalts a continuous pressure still cracked residuum having an A. P. I. gravity of 7.8°, a flash of 340° F., a Furol viscosity at 122° F. of 227 seconds, and a pourpoint of +35° F. and showing a positive spot test was admixed with various amounts of a propane insoluble asphaltic resin of the type used in Example I. It was found that 70% of the propane-insoluble asphaltic resin was required to obtain a negative spot test. While a relatively large amount of the asphaltic resin was required, it is unexpected that a negative spot test can be obtained at all on an asphalt containing as much as 30% of a cracked product since the spot test was originally designed to indicate the presence of any cracked products in asphaltic materials.

Frequently, petroleum bitumen composition, such as asphalts, cut-back asphalts, road oils, and the like, used for paving and road building, are compounded with various additives, such as anti-stripping agents. Such additives are used to facilitate the application of paving materials and road oils to wet mineral aggregates and to prevent the stripping of such materials from wet aggregates. Examples of such additives are metal salts of sulfonic acids, naphthenic acid, high molecular weight fatty acids, as well as fats and fatty material, such as the propane-insoluble residue obtained from the propane fractionation of crude fatty materials. Particularly effective additives are calcium petroleum sulfonates. In many cases difficulty is experienced in keeping such additives in stable suspension or solution, in the bitumen material. We have found that the addition of up to 35%, by weight, of the asphaltic resins insoluble in liquefied normally gaseous hydrocarbons, for example, propane, is very effective in stabilizing such compositions against separation of the anti-stripping agents.

While we have described our invention by reference to specific examples thereof, these have been by way of illustration only and the invention is not to be limited thereby but includes within the scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. The method of converting a positive spot test petroleum bitumen material to a negative spot test product, comprising admixing with a petroleum bitumen material normally having a positive spot test, an untreated asphaltic resin insoluble in a liquefied normally gaseous hydrocarbon obtained from the deasphalting of a petroleum residuum normally exhibiting a negative spot test with a liquefied normally gaseous hydrocarbon, said untreated asphaltic resin being present in a small but sufficient quantity to give the resultant product a negative spot test.

2. The method of converting a positive spot test petroleum asphaltic material to a negative spot test product, comprising admixing a petroleum asphaltic material normally exhibiting a positive spot test with an untreated propane-insoluble asphaltic resin obtained from the propane deasphalting of a petroleum residuum normally exhibiting a negative spot test, said propane-insoluble asphaltic resin being used in small but sufficient quantities to impart to said petroleum asphaltic material a negative spot test.

3. The method of claim 2 in which the propane-insoluble asphaltic resin is used in amounts within

the range of from about 0.5% to about 15%, by weight.

4. The method of correcting the heterogeneity of a petroleum asphaltic material comprising admixing with a petroleum asphaltic material normally having a positive spot test, from about 0.5% to about 15%, by weight, of untreated propane-insoluble asphaltic resins obtained in the propane deasphalting of a petroleum residuum normally exhibiting a negative spot test.

5. The method of preparing a petroleum asphaltic product having a negative spot test comprising admixing a petroleum asphaltic material normally having a positive spot test with from about 0.5% to about 15%, by weight, of untreated propane-insoluble asphaltic resins, obtained from petroleum residuums normally having a negative spot test.

6. The method of converting a positive spot test asphalt to a negative spot test asphalt, comprising incorporating in a positive spot test asphalt from about 0.5% to about 15%, by weight, of untreated propane-insoluble asphaltic resins obtained by propane deasphalting a petroleum residuum normally having a negative spot test.

7. A petroleum asphaltic composition having a negative spot test comprising a major proportion of a petroleum asphaltic material normally having a positive spot test and a minor proportion of untreated asphaltic resins insoluble in liquefied normally gaseous hydrocarbons obtained from the deasphalting of a bitumen residuum normally having a negative spot test with a liquefied normally gaseous hydrocarbon, said asphaltic resins being present in small but sufficient quantities to impart to said composition a negative spot test.

8. A petroleum bitumen composition having a negative spot test comprising a major proportion of a petroleum bitumen normally having a positive spot test and from about 0.5% to about 15%, by weight, of an untreated propane-insoluble asphaltic resin obtained in the propane deasphalting of a bitumen residuum normally having a negative spot test.

9. A petroleum asphalt composition having a negative spot test comprising a major proportion of a petroleum asphalt normally having a positive spot test and from 0.5% to about 15%, by weight, of untreated propane-insoluble asphaltic resins obtained by the propane deasphalting of a petroleum residuum normally having a negative spot test.

10. A road oil composition having a negative spot test comprising a major proportion of a petroleum residuum normally having a positive spot test and from about 0.5% to about 15%, by weight, of an untreated propane-insoluble asphaltic resin obtained by the propane deasphalting of a petroleum residuum normally having a negative spot test.

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